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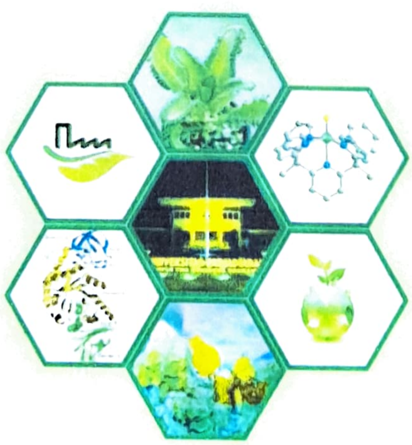

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Kinetics and adsorption isotherms of zeolite-MBT selective adsorbent towards Cd(II) ions in mixed systems

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Abstract

The adsorption of Zeolite-MBT toward Cd(II) Ion in mixed systems has been investigated in batch mode. Effect of time and initial concentration of adsorbent on metal ion selective adsorption was investigated. The zeolite-MBT adsorbent was synthesized previously by impregnation of MBT to zeolite dealumination at at pH 8, temperature 80°C and zeolit-MBT ratio is 0,12. The result showed that the adsorption of zeolite-MBT to Cd(II) ion in mixed system favourable the first-order kinetic model with correlation coefficient, R^2 are 0.758 and 0.635 respectively for CdII) and Cr(III) metal ions. Freundlich's and Langmuir's mathematical models were used to describe batch adsorption equilibrium data and the constant of adsorption were evaluated. The adsorption was found to be favourable in both isotherms. The corelation coefficient, R^2 of Langmuir isoterm are 0.993 and 0.929, and the Freundlich's isoterm are 0.943 and 0.920 respectively for Cd and Cr metal ions.

Keywords: Kinetics, adsorption Isotherms, selective adsorption, Zeolite-MBT

Introduction

Many industrial processes produce aqueous effluents containing toxic metal contaminants. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In particular, cadmium and cadmium compounds are especially dangerous and highly toxic. Cadmium toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer and diabetes. Cadmium concentrates in the kidney, liver and various other organs and is considered more toxic than either lead or mercury (El-Sayed *et al.*, 2010).

Recovery of heavy metal from wastewater and industrial waste has become a very important environmental issue (Saravanan etal., 2009; Ghazy *et al.*, 2008). Inorganic effluent from the industries contains toxic metals such as Ni, Cu, Zn and Cd which tend to accumulate in the food chain. Because of their high solubility in the aquatic environments, heavy metal can be adsorbed by living organism. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. Therefore, it is necessary to treat metal contaminate wastewater prior to its discharge to the environment (Panneerselvam *et al.* 2009; Kurniawan *et al.* 2006).

Many processes for the removal of heavy metals from water and wastewater have been investigated (Panneerselvam *et al.* 2009; Buasri *et al.*, 2008; Kurniawan *et al.* 2006). Various treatments have been developed for purification of water and wastewater contaminated by heavy metals, including precipitation, coagulation – flocculation, electrochemical treatment, chelation, biosorption, adsorption, membrane filtration, solvent extraction, reverse osmosis, and ion exchange model (Lesmana et al., 2009; Panneerselvam *et al.* 2009; Vázquez, 2009; Barakat, 2008; and Kurniawan *et al.*, 2006).

Efforts to adsorb of heavy metal ions in the environment by using natural materials have been widely reported. Buasri at.al (2008) using natural zeolite Clinoptololit to remove Pb (II) from wastewater. Halima Husain and Ramlawati (2007) using natural zeolite to reduce the levels of peroxide in cooking oil.

Optimization of the purification process of waste materials or require development of new materials based on the availability of raw materials are plentiful and inexpensive and has a high effectiveness in removing heavy metals. The complexity types of industrial wastes require proper handling techniques.

The use of natural zeolite as an adsorbent for the adsorption of heavy metals in waste water has been done, because the zeolite qualified as a good adsorbent, cheap and easy to find. However, in some cases, to a certain practical purpose is to be collected or separated from one or several specific metals in mixed metal waste system, sometimes less selective use of natural zeolite as separation power is still relatively low (Tsitsishvili et al, 1992). One method that is being developed to increase selectivity is to modify the surface of natural zeolite by impregnation with certain organic materials. The organic materials have been impregnated into zeolite characterized favourable to bond with one or several specific metal ions than other, hence resulting a selective adsorption.

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Some of the researches related to the impregnation process has long pioneered. It can be concluded that adsorbent materials modified by impregnation techniques have adsorption capacity and better selectivity for adsorption purposes especially depending on the type of metal adsorbate and the functional group in organic matter. Merkaptobenzotiazol an abbreviated 2-MBT is the molecular formula $C_7H_5NS_2$ impregnant material which has high stability and selectivity towards certain metal ions.

The impregnation is entering process of material to porous of the pellets by using the physical interaction between the pore with physics interaction impregnant material. Interactions that occur in the adsorption of metal ions by the adsorbent impregnation results in zeolite-MBT, is expected to involve the thiolate group (RS-) from MBT. The negatively charged thiolate groups have a great affinity to interact with positively charged metal ions. Thus, the interaction between the MBT with adsorbate metal ions is seen as a Lewis acid-base interactions that form a complex on the surface of solids (Amri *et al.* 2004).

Based on the classification Pearson acid-based, active situs on solid surface could be assumed as ligan which could bond the metal selectively. Metal and ligan are grouped according to characteristic of elements polarizability. Pearson (1963) said that the principle is *Hard and Soft Acid Bases (HSAB)*. Ligands with highly electronegative atoms and small size is a strong base, while the ligands with their valence electrons of atoms are easily polarized under the influence of ions from the outside is a weak base.The outer electron of small metal ions isn't influenced by outer ion, this is grouped into strong acid, while the big one is strong base

According to Pearson's *hard soft* [Lewis] acid base (HSAB) principle: *Hard* [Lewis] acids prefer to bind to *hard* [Lewis] bases and *Soft* [Lewis] acids prefer to bind to *soft* [Lewis] bases (http://www.meta-synthesis.com/ webbook/ 43_hsab /HSAB.html). At first sight, HSAB analysis seems rather similar to the **Type A** and **Type B** system. However, Pearson classified a very wide range of atoms, ions, molecules and molecular ions as *hard, borderline or soft* Lewis acids or Lewis bases, *moving the analysis from traditional metal/ligand* inorganic chemistry into the realm of organic chemistry.

Pearson's HSAB Classification System, from Table 1 for classification of Lewis acids and Table 2 for classification of Lewis bases.

Table 1 Classification of Lewis Acids

Class (a) Hard	Class (b) Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	CH_3Hg^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	Tl^{3+}, $Tl(CH_3)_3$, RH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	RS^+, RSe^+, RTe^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I^+, Br^+, HO^+, RO^+
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	I_2, Br_2, ICN, etc
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Trinitrobenzene, etc
RPO_2^+, $ROPO_2^+$	Chloranil, quinones, etc
RSO_2^+, $ROSO_2^+$, SO_3	Tetracyanoethylene, etc
I^{7+}, I^{5+}, Cl^{7+}	O, Cl, Br, I, R_3C
R_3C^+, RCO^+, CO_2, NC^+	M^0 (metal atoms)
	Bulk metals
HX (hydrogen-bonding molecules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	

The grouping of Lewis acid-base through to the HSAB Pearson principle, hard acid will interact with hard base to form complex, and it also happened for soft acid-base. Interaction of hard-acid with hard-base is ionic interaction, while soft acid interaction with soft base, and the interaction is in covalent. In this research, impregnated MBT on zeolit consists of weak base of thiolat (R-SH). The interaction of thiolate with metal had to be happened as suitable with HSAB Pearson's principle.

Table 2 Classification of Lewis bases

Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-
Borderline	
$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2	

Based on these principles, then the 2-merkaptobenzotiazol impregnan expected to interact strongly with the metal ions form a soft acid than covalent bonds with metal ions characterized by strong acids. The model of interaction between the zeolite-MBT with metal ions can be seen in Figure 1.

Based on the background and theory, in this study will be reviewed and the kinetics of zeolite-MBT adsorption isotherms of Cd ions in the mixed system.

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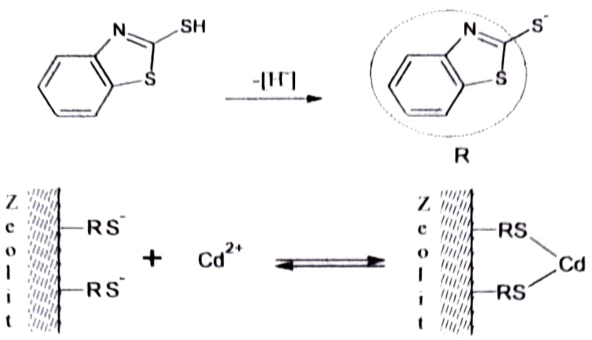

Figure 1 The interaction between the zeolite-MBT with Cd(II) metal ions. Source: Amri, *et al.* (2004)

Materials and Methods

Materials

The materials of the research, are:: zeolite sampel from Sangkaropi Saddang Balusu Sub-district, Toraja Utara District, 2-mercaptobenzothiazol, buffer citric-sodium hydrogen phosfat, $Cd(NO_3)_2$. 4 H_2O, $Cr(NO_3)$.9 H_2O. The apparatus are: Shakerbath, Ball mill, oven, Water bath, AAS, dan FTIR.

Preparation of zeolit-MBT

The zeolites +100-150 mesh dealuminated by adding 100 ml of 6 M H_2SO_4 and 100 ml of 0.5 M $KMnO_4$, then heated for 4 hours at 80 ° C with gently stirring over a hot plate. Furthermore, the zeolite was washed until neutral, and dried at 80 ° C for 12 hours. Zeolite obtained coupled with 100 ml of 6 M H2SO4 and heated at 80 ° C for 5 hours with stirring gently, then washed with aquades to neutral. After that, the sample was added 150 ml of 6 M HCl and heated at 80 ° C for 3 hours with stirring gently, and then washed again until neutral pH and dried at 80 ° C for 12 hours (Amri, et al, 2004). Furthermore, zeolite impregnated with MBT in optimum conditions of impregnation at pH 8, temperature 80°C with zeolite-MBT ratio of 0.12 (Ramlawati and Darminto, 2009). The results obtained so-called zeolite-MBT.

Characterization of Zeolit-MBT

Characterization of zeolite-MBT interaction with metal ions used FTIR, namely by comparing the FTIR absorption spectra of zeolite-MBT by absorption spectra of zeolite-MBT metal-ion.

Determination of adsorption kinetics of zeolite-MBT to Cd(II) ions in mixed method

Zeolite-MBT was interacted with metal ion in mixed solution of Cd-Cr at pH 7 and the ratio (zeolite-MBT)-adsorbate solution 0.03. MBT zeolite-time interaction with metal ions Cd in binary mixture was varied, ie 60, 120, 180 and 240 minutes. Each treatment was made triplo.

The equation of first-order (1) and second order (2) kinetics are used are:

$$k = \frac{1}{t} \ln \left(\frac{a}{a-x}\right) \quad \text{.......... (1)}$$

$$k = \frac{1}{t} \left(\frac{x}{a(a-x)}\right) \quad \text{.......... (2)}$$

Where:

k = *rate constants*
t = *time of reactions*
a = *initial concentration (mg/L)*
x = *final concentration (mg/L)*

Determination of adsorption isotherm

The pattern of adsorption isotherms are determined through the interaction of zeolite-MBT on different variations of the initial concentration. A certain amount of zeolite-MBT mixed with a solution of a mixture of Cd metal ions in binary mixtures diinteraksikan for 3 hours at pH 7 and the ratio of the zeolite-adsorbate solution of 0.03. Initial concentration of metal ion mixtures varied, namely 10, 25, 50, 100 and 150 mg/L. The amount of metal ions adsorbed on the zeolite-MBT was analyzed by AAS. The amount of cadmium adsorbed on zeolite-MBT was analysis by AAS. Each treatment was made triplo.The amount of cadmium adsorbed was taken as the difference the between the amount taken And that found in the filtrate on equilibration after making due Corrections for the cadmium and chromium ions present in the entrapped solution.

From the above measured data, sorption kinetics, Langmuir's isotherm and Freundlich's parameters were evaluated. The cadmium ion uptake in biner mixed was calculated using the following mass balance equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad \text{.......... (3)}$$

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Where

q_e or x/m = metal ion uptake (mg metal ion/ g adsorbent)

V = Volume of metal ion solution in contact with adsorbent(L)

C_o = Initial concentration of metal in solution (mg/L)

Ce = Final Concentration of metal in solution (mg/L)

S = Dry weight of the adsorbent (g)

The pattern of zeolite-MBT adsorption can be tested against patterns suitable with Freundlich and Langmuir adsorption isotherms. Equation of Freundlich and Langmuir adsorption isotherms are respectively as follows:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \quad (4)$$

Where:

X = amount of metal ion was adsorbed (mg/L)

m = amount of adsorbent (g)

c = equilibrium concentration (mg/L)

k dan n = konstanta

$$\frac{c}{q} = \frac{1}{bK} + \frac{1}{b}C \quad (5)$$

Where:

C =equilibrium concentration (mg/L)

q = amount of metal ion was adsorbed (mg/g)

b and K = konstanta

Adsorption capacities (b) = *slope*

K and b should be complicated by slope and intersep of diagram (Oscik, 1982).

Results and Discussions

Characterization of zeolite-MBT

The success of MBT impregnation on zeolite can be identified in the FTIR spectra of zeolite-MBT (Figure 2. The typical absorption spectra of MBT at a wavelength of 1595 cm^{-1} of the C = C aromatic, C = C aromatic weak at a wavelength of 1639 cm^{-1}, CH aromatic strec at ± 3000 cm^{-1}, CH def absorption at a wavelength of 848 and 866 cm^{-1}, aryl-SH absorption at a wavelength of 2505.4 cm^{-1}, CS absorption at 603.7 cm^{-1}, CN absorption at 1319 cm^{-1}.

Effect of contact time and adsorption kinetics

Effect of contact time of zeolite-MBT adsorption of metal ions Cd in the mixed system is shown in Figure 3. In the picture looks a maximum adsorption for Cd and Cr metal ions occurs in the range of 3-4 hours.

The adsorption kinetics of metal ions in zeolite-MBT has been tested by evaluating the enforceability of the metal ion adsorption data at various contact time. Validity of data on the kinetics of first order equations and second-order two metal ions can be seen in Figure 4 (a) and 3 (b).
In summary the coefficient of determination (R^2) is great for both metal ions, then to order kinetics first and second-order zeolite ion-MBT of Cd ions in a mixture of beer can be seen in Table 3.

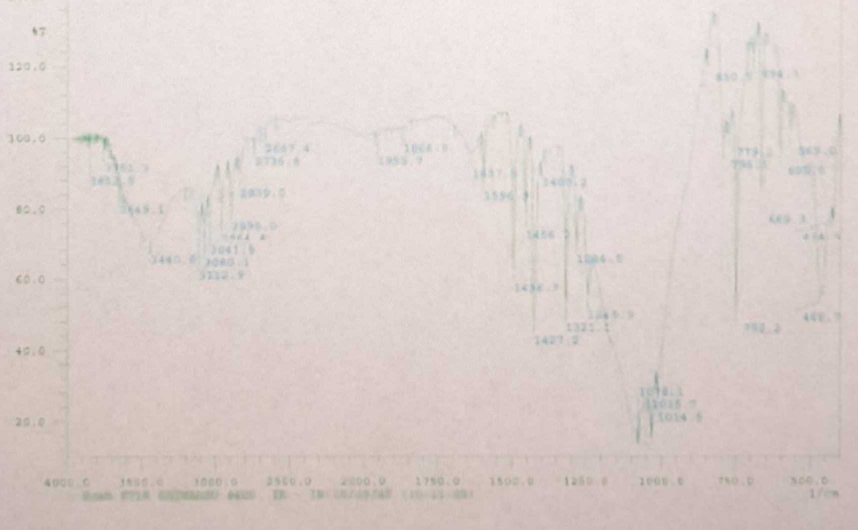

Figure 2 FTIR spektra of zeolit-MBT

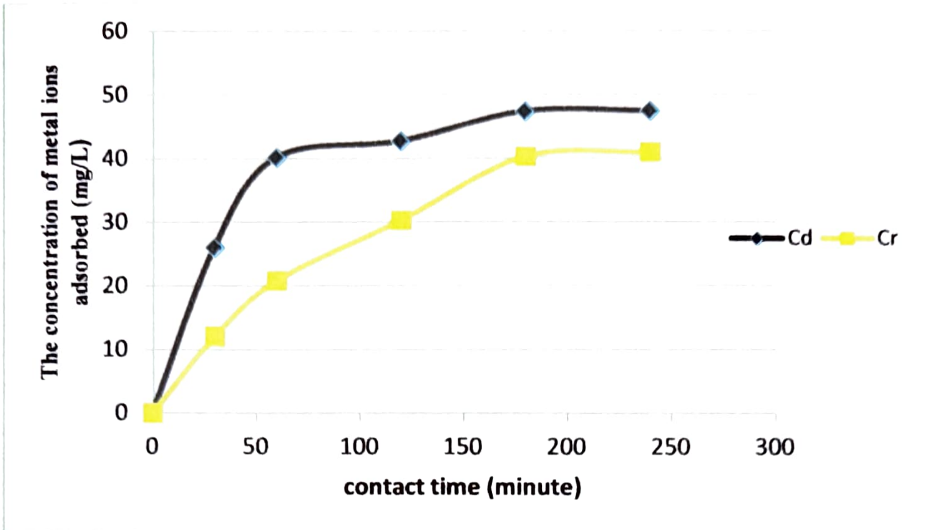

Figure 3 Effect of contact time on the adsorption of zeolite-MBT

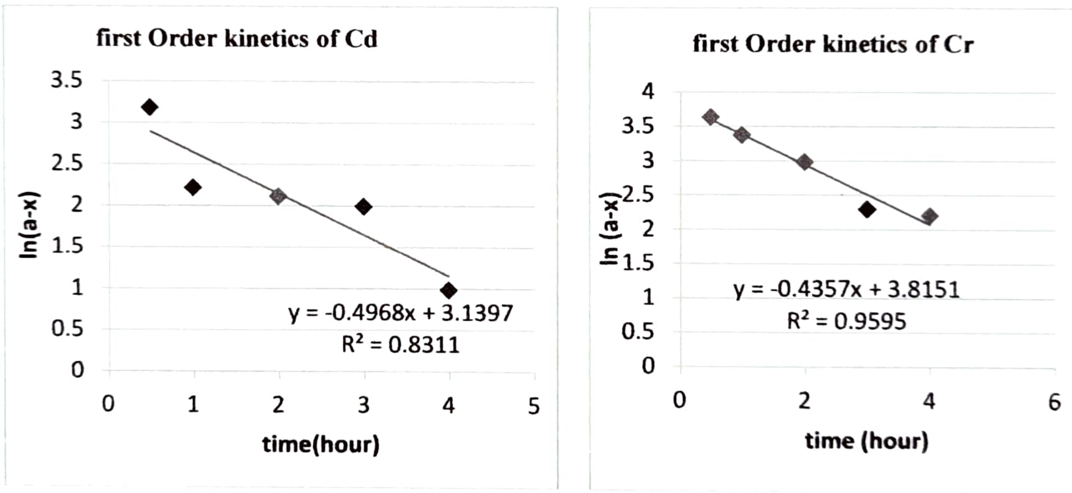

Figure 4 Graph order-kinetics of the adsorption of zeolite-MBT to Cd and Cr ions

In Table 3, it appears that the adsorption of both Cd(II) and Cr(III) ions on zeolite-MBT are pseudo-first- and pseudo-second order kinetics.

Table 3. Coefficient of Determination Zeolite Adsorption Kinetics of Ion-MBT Cd in Binary Mixture

Equation	Koef. determinasi (R^2)	
	Metal Ion Cd(II)	Metal ion Cr(III)
First Order Kinetics	0.831	0.960
Second Order Kinetics	0.763	0.947

Effect of initial concentration and adsorption isotherm

Initial concentration of metal ions in the mixed system affecting the adsorption of MBT on the zeolite-metal ions. Data obtained from these variables can be used to determine the pattern of adsorption of metal ions in zeolite-MBT. The pattern of zeolite-MBT adsorption on ion Cd(II) and Cr(III) can be seen in Figure 5

The increases of the initial concentration followed with increasing amount of metal ions adsorbed on the zeolite-MBT. The amount of adsorbed metal ions is almost constant at the initial concentration of 100 to 150 mg / L.

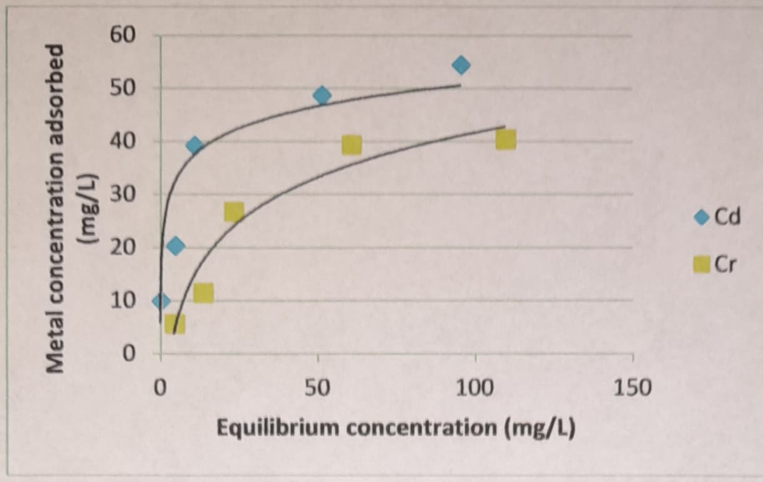

Figure 5 Adsorption isotherm of zeolit-MBT to Cd and Cr ions

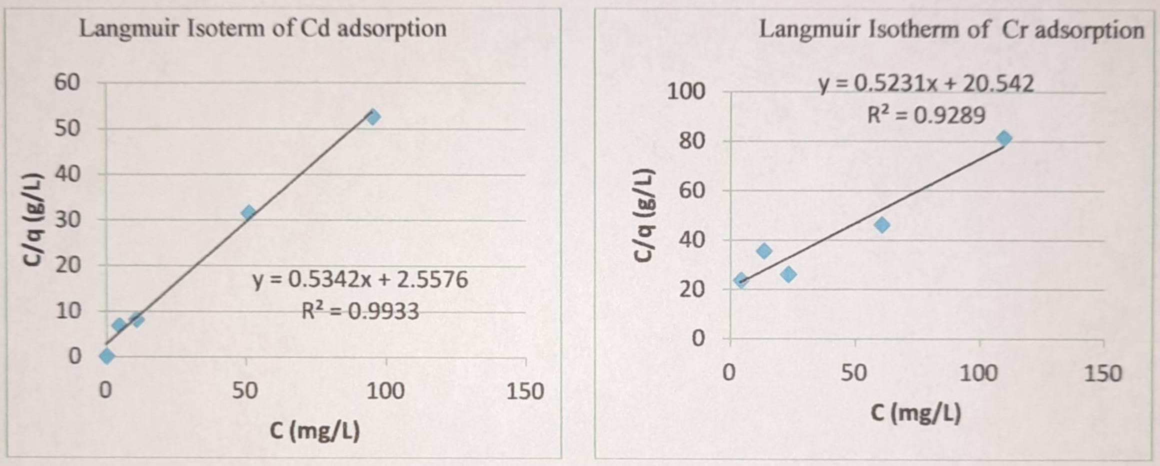

Figure 6 Langmuir Isotherm of Cd and Cr Adsorption on Zeolite-MBT

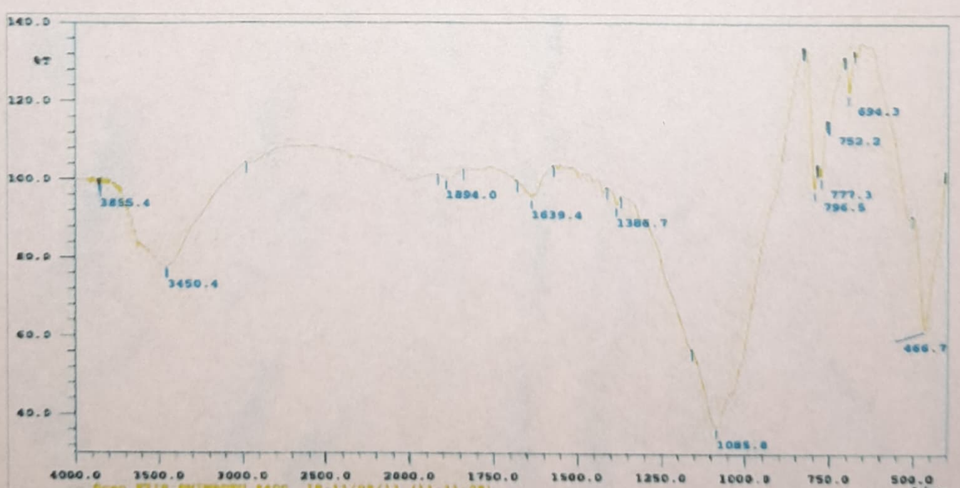

Figure 7 FTIR spektra of interraction between zeolit-MBT and Cd(II)

The initial concentration of metal ions affect the adsorption of zeolite-MBT. The data obtained show that the pattern of metal ion adsorption of Cd and Cr suitable Langmuir isotherm pattern, namely the occurrence of single-layer adsorption in which the initial concentration increases at a certain concentration does not lead to an increased amount of adsorbed metal ions. This occurs because the surface of the adsorbent was charged metal ions. Validity of data on the pattern of the Langmuir isotherm can be seen through the graph in Figure 6 (a) and 6 (b).

Langmuir isotherm patterns indicate that the interactions that occur between the adsorbent and adsorbate occurs on the surface. Interactions of this type occurs when there is a strong interaction between adsoben and adsorbate (Oscik, 1982).

The existence of strong interactions that occur between Cd ions and Cr ions in zeolite-MBT can be seen in FTIR spectra are in Figure 2.7 and 8. In the Figure 6 it appears that the spectra of aryl-SH groups at a frequency of 2505cm^{-1} no longer appears FTIR spectra of zeolite-MBT-Cd spectra and zeolite-MBT-(Cd-Cr). The C=C aromatic group of MBT and the spectra of Si-OH at 3411 cm-1 frequency appear sharply in the spectra of zeolite-MBT-Cd-Cr.

The high adsorption thiolat other than caused by the negatively charged groups are also caused by the negatively charged silanol groups. As stated by the isoelectric point (IEP) for silica Occurs at approximately pH 2, and is somewhat dependent on the exact nature of the surface. The density of negative charges remains low until the solution pH reaches 6, but increases sharply the between pH 6 and 11 (Koopal and Goloub (in Atkin et al. 2003).

Conclusions

The results showed that the adsorption of zeolite-MBT toward Cd^{2+} ions in biner mixed that zeolite-MBT is an efficient as selective adsorbent media for the removal of cadmium ions from biner mixed in aqueous solution and wastewater. The removal efficiency increases with the increase of contact time and initial concentration. The adsorption isotherm data fit well with Langmuir isotherm while the kinetic data were represented by pseudo-first and second—order kinetic model. The impregnation of zeolites can very well be recommended for selective adsorption of cadmium in wastewater treatment and control of environmental pollution.

Acknowledgements

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Figure 8 FTIR spektra of interraction between zeolit-MBT- (Cd-Cr)

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